

The influence of mechanical activation on zinc stannate spinel formation

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Abstract

Mechanical activation of inorganic materials leads to specific changes of their chemical and physical properties. Grinding, as one way of mechanical activation, is a widely used method for obtaining highly dispersed systems, and it could be performed in various types of mills (planetary, centrifugal, vibro-mill, etc.). The development of advanced materials is, therefore, dependent not only on the investigated material, but on characteristics of a device as well. Polycrystalline zinc stannate spinel, Zn_2SnO_4 , is a material used for combustible gases and humidity detection, photoelectrochemical applications, coatings, etc. The subject of this work is the influence of mechanical activation on solid state chemical reaction, e.g. the formation of porous zinc stannate ceramics during different thermal treatments of compacts obtained from ZnO and SnO_2 powder mixtures mechanically activated in a high energy vibro-mill. X-ray diffraction analysis, scanning electron microscopy and non-isothermal dilatometric measurements were performed in order to investigate spinel formation. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Zinc oxide (ZnO) and tin oxide (SnO_2), *n*-type semiconductors, are mainly used as materials for manufacturing of electronic parts. Recently, special attention has been paid to the ZnO – SnO_2 system due to specific electrical properties of polycrystalline zinc stannate, Zn_2SnO_4 . Zinc stannate with a spinel structure can be exploited in the production of sensors for detection of moisture and various combustible gases.

Only a small number of investigations have been performed on this subject so far. Hashemi¹ studied the synthesis of spinel by the solid state reaction of ZnO and SnO_2 , while Hiratsuka² synthesized zinc stannate by the sintering of mechanically activated mixtures with the addition of camphor. Thin films of Zn_2SnO_4 for moisture detection were also obtained by spray pyrolysis,³ or synthesized by vacuum vapor deposition that showed high sensitivity to NO_2 .⁴

Mechanical activation by grinding, as a method for modifying the physico-chemical properties of dispersed materials, is often used in powder technology.^{5,6} Specific changes that occur during grinding have a great influence on final properties of the obtained material, thus implying their specific application. Grinding could be performed in various types of mills, while vibro-mills are used for efficient fine grinding of metal and ceramic powders. Mechanical activation by grinding is an assemblage of processes and mainly occurs in four stages: material destruction, formation of a new surface on the material which is destroyed, fine grinding and transformation into a new material with a completely different structure.⁵ Mechanical activation by grinding of the ZnO – SnO_2 system was studied in order to obtain the optimal conditions for zinc stannate (Zn_2SnO_4) synthesis. It is a common fact that the establishment of the desired sensor properties requires obtaining and controlling of a materials microstructure. Since grinding could lead not only to a reduction of crystallite size, but also to the deformation/change of a crystal structure, the influence of activation (grinding) time on spinel formation and evolution of microstructure was investigated in this work.

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Reaction sintering is a process between two or more phases (active powders) that results in the formation of a new phase by a solid state reaction.⁷ It could also be defined as a process during which a chemical reaction and sample densification take place simultaneously.⁸ Mechanical activation of powders during grinding improves their reactivity and further accelerates the solid state reaction. Since reaction sintering of ZnO and SnO₂ powder mixtures can take place due to different mechanisms and external influences, the influence of powder history (mechanical activation) on zinc stannate spinel formation was investigated in this work.

2. Experimental

Mixtures of ZnO and SnO₂ powders (p.a.), with the molar ratio of ZnO:SnO₂=2:1, were mechanically activated by grinding in a vibro-mill (KHD Humboldt Wedag AG, MH954/3) in the time range of $t_{AC}=0$ –160 min. Determination of specific surface areas was carried out using the BET method with N₂ adsorbate. X-ray diffraction (XRD) analysis of powders (non-activated and activated) and sintered samples was performed using a PHILIPS 1820 diffractometer with CuK $_{\alpha 1/2}$ radiation and a graphite monochromator. The step scanning mode was 0.02°/s. The relative shrinkage of samples obtained by uniaxial pressing of activated powders was followed by sensitive dilatometer (Bähr Gerätebau GmbH Typ 702 s) during non-isothermal heating in air up to 1200°C with a constant heating rate (10°C/min). Different compaction pressures were applied in order to obtain green compacts with approximately the same density for all activated powder mixtures (0.52–0.56 ρ_t , where $\rho_t=6.42$ g/cm³ is the theoretical density of zinc stannate). The morphology of sintered samples was examined by scanning electron microscopy (JSM 5300-Jeol, 30 kV).

3. Results and discussion

Previous investigations of the mechanical activation effects on the sintering process showed an intensification of both the sintering process and solid state reaction with prolonged grinding time.⁶ In fact, it was noticed that the activation process leads to changes in the specific surface of initial powders. This is the consequence of destruction of agglomerates (it is well known that ceramic powders are mainly agglomerated) and the particle comminution of the starting materials. The specific surface values of 20.27, 22.60, 25.70, 29.15 and 27.15 m²/g⁻¹ were obtained for non-activated and powder mixtures activated for 10, 40, 80 and 160 min, respectively. According to this, a small decrease of specific surface after activation for 160 min can be ascribed to the re-agglomeration. It should be emphasized that particle and agglomerate fragmentation

during grinding, as well as the formation of new fragments (agglomeration) and the mechanochemical reaction represent the specific means of energy dissipation. Grinding of particles increases system entropy, while solid state reactions (the formation of Zn₂SnO₄) lead to energy loss. Therefore, optimization of the time of activation, solid state reaction and sintering parameters is necessary for obtaining a desired material in an optimal technological regime.

To provide informations about the influence of activation on solid state reaction, XRD analysis was performed in order to analyse changes of phase composition. Fig. 1 shows X-ray diffraction patterns of the examined ZnO–SnO₂ system. The XRD pattern of the starting powder mixture (Fig. 1a) shows the presence of hexagonal ZnO and tetragonal SnO₂. XRD analysis of activated mixtures showed that during grinding of the ZnO–SnO₂ powders mixture in a high energy vibro-mill in the examined experimental range only changes of shape, width and relative intensity of characteristic ZnO and SnO₂ diffraction lines occurred. Spinel phase formation, i.e. mechanochemical effect, was only observed as one insignificant diffraction line in the mixture activated for 160 min. A detailed analysis of data of activated powder mixtures obtained from XRD measurements was described elsewhere.⁹ The appearance of a new phase (zinc stannate) in the XRD pattern is evident for the sintered non-activated sample ($t_{AC}=0$ min), as shown in Fig. 1b, including the existence of an insignificant amount of residual ZnO and SnO₂. The sintered sample activated for 10 min (Fig. 1c) shows that the reaction proceeds towards the formation of zinc stannate. When the time of activation is increased up to 160 min (Fig. 1d), XRD

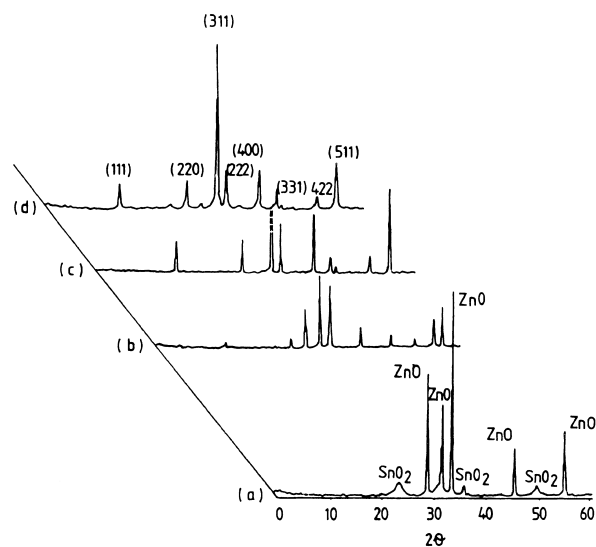


Fig. 1. X-ray diffraction patterns of the ZnO–SnO₂ system (2:1): (a) starting powder mixture; samples sintered at 1200°C for 2 h with a heating rate of 10°C/min obtained from mixtures activated for (b) 0 min, (c) 10 min and (d) 160 min [characteristic diffraction lines of zinc stannate indicated at (d) refer to (b) and (c) as well].

results indicate that polycrystalline spinel (Zn_2SnO_4) is formed with no evidence of another phases within the diffractometer experimental error.

Analysis of dilatometric measurements provided more important informations about the sintering process and, in this case, also about solid state reactions. The influence of activation time on relative shrinkage of ZnO-SnO_2 samples during non-isothermal heating up to 1200°C is presented in Fig. 2. As it could be seen in Fig. 2, the shape of dilatometric curves is quite different for non-activated and activated thermally treated samples. Characteristic temperatures obtained from analysis of dilatometric data are given in Table 1. The analysis of samples relative shrinkage indicate that samples prepared from mixture activated for 160 min have the most intensive shrinkage. This is the consequence of the increase of the ZnO-SnO_2 powder mixtures reactivity observed during mechanical activation by grinding, reflected on the properties of a sintered sample, as well. The influence of mechanical activation is quite evident for all activated samples, and is manifested by the different shapes of dilatometric curves. The temperature that marks the beginning of a chemical reaction between zinc oxide and tin oxide (according to the literature data¹), T_{\min} in Table 1, moves towards lower temperatures with the increase of the activation time. The beginning of intensive relative shrinkage of samples depends on the activation time (Fig. 2 and T_{\max} in Table 1) in the same way as

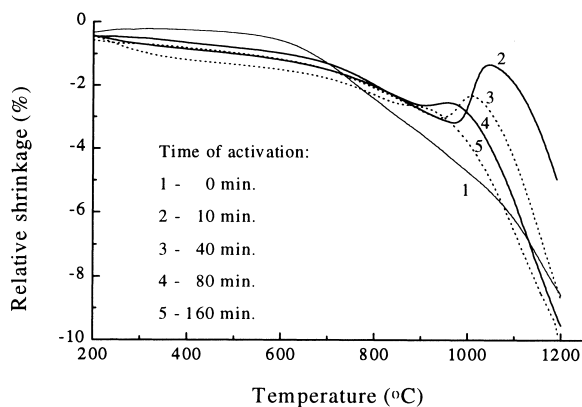


Fig. 2. Relative shrinkage of samples as a function of the heating temperature for different times of activation.

Table 1
Characteristic temperatures obtained from analysis of dilatometric data

| Time of activation (min) | T_{\min} ($^\circ\text{C}$) | T_{\max} ($^\circ\text{C}$) |
|--------------------------|---------------------------------|---------------------------------|
| 0 | 1085 | — |
| 10 | 975 | 1050 |
| 40 | 945 | 1010 |
| 80 | 900 | 965 |
| 160 | 845 | 925 |

T_{\min} . Chemical reaction is accompanied by a sample expansion while sample shrinkage occurs during sintering, where these two processes proceeds simultaneously. With the increase of activation time, intensive shrinkage starts at a lower temperature and becomes a dominant process. This could be the explanation for smaller characteristic expansion. That also points to the increase of reaction rate with the increase of the time of activation. In this way, sintering temperature could be significantly lowered by performing an optimal activation, for example, zinc stannate formation at 925°C for mixtures activated for 160 min, which represent a lower sintering temperature than the one reported in the literature.¹

The structure of a ceramic-based sensor material should be porous. Sensor sensitivity and response time are determined by the material itself (composition, structure), preparation method and sintering conditions. Since the control of microstructure plays a significant role in the stability and reliability of sensor-based materials,¹⁰ control of porosity is also of great importance.

The evolution of microstructure during sintering with respect to the time of activation is presented in Figs. 3–5. SEM microphotographs of fractured samples obtained from different mixtures sintered at 1200°C for 2 h revealed that samples are porous and that the microstructures are affected by the time of activation, which is in accordance with previous investigations of the ZnO-SnO_2 system.⁹ Agglomeration of initial, non-activated powders with different particle shapes and sizes is probably preserved in sintered samples. Thus, it can be concluded that initial powder mixtures contain agglomerates and that their behavior during compaction and sintering inhibits solid state reactions and the materials densification. On the contrary, the activated powder mixtures contain smaller particles that promote solid state reactions and densification.

Based on the analysis presented in this work, porous zinc stannate spinel formation could be performed through the following stages: mechanical activation

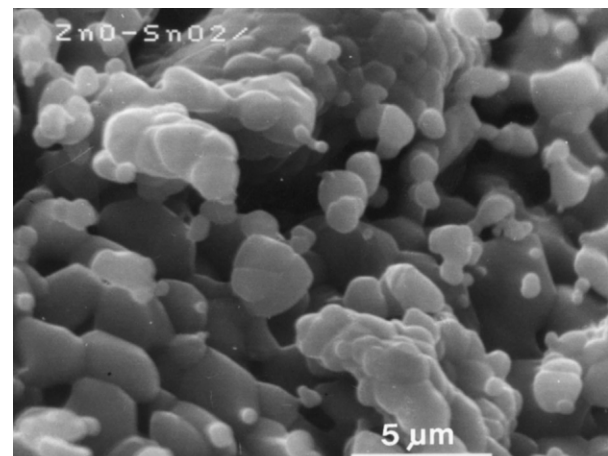


Fig. 3. SEM of the fractured sintered sample ($t_{\text{AC}}=0$ min).

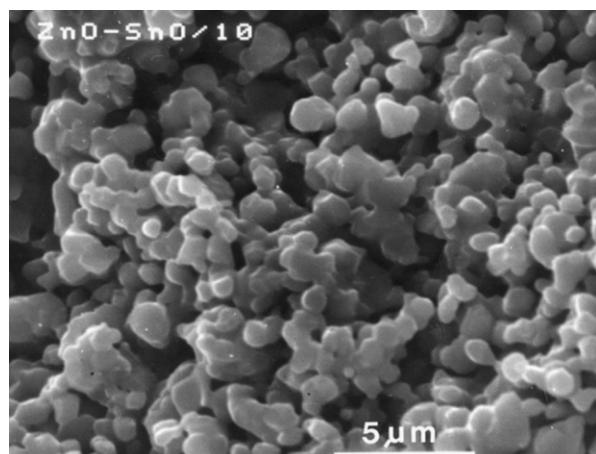


Fig. 4. SEM of the fractured sintered sample ($t_{AC} = 10$ min).

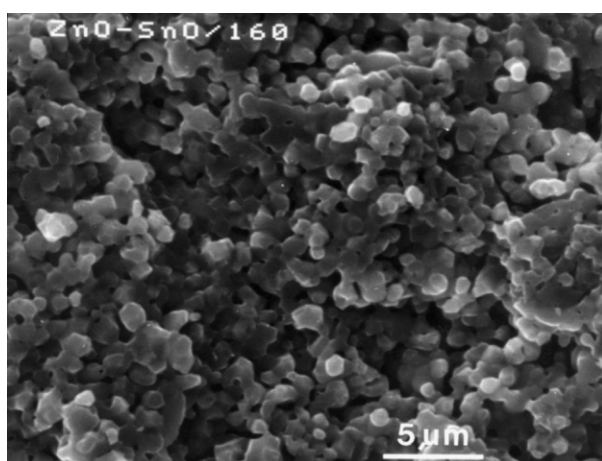


Fig. 5. SEM of the fractured sintered sample ($t_{AC} = 160$ min).

($t_{AC} > 10$ min) and isothermal sintering at temperatures higher than 1100°C for a few hours. The established result points out to obtaining of zinc stannate spinel ceramics at temperatures much lower than 1280°C , which is that reported in the literature.¹

4. Conclusion

The synthesis of polycrystalline zinc stannate by a solid state reaction and the influence of mechanical activation on its formation were studied in this work. It was established that zinc stannate reaction rate could be enhanced by prolonged grinding, i.e. time of activation. It

was shown that the increase of the activation time significantly modifies the sintering behavior of the examined ZnO–SnO₂ system. The temperature for the formation of zinc stannate depends on the time of activation. Monophased polycrystalline zinc stannate was formed when the samples activated for 160 min were sintered at 1200°C for 2 h. Based on the obtained results, an strategy for the formation of porous zinc stannate by a solid state reaction was established.

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